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CHEMICAL KINETICS OF SOLID PROPELLANTS

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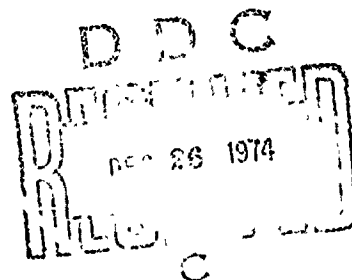
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### Abstract

In this report we summarize the results obtained in our experimental and theoretical work on the chemical kinetics of solid propellants. These studies concerned the reaction kinetics of the condensed phase, of the gas/solid interface, and of the gas phase involving ammonium perchlorate organic fuels, and metal-oxide catalysts. The data allow an evaluation of the reaction kinetics in the different phases to the ignition and deflagration of solid propellants based on ammonium perchlorate.

## INTRODUCTION

The advances made in the development of operational solid propellants based on ammonium perchlorate (AP) have not been matched by detailed understanding of the processes occurring during deflagration, ignition, and extinction. As a result, further technological progress is impeded by the absence of a firm base of theoretical knowledge to guide the engineer. Of major concern is the elucidation of those processes that control the rate of conversion of chemical to thermal energy in a complex propulsion system having for its principal ingredients AP, catalyst, fuel binder, and various metal-containing additives.

It has become increasingly apparent that a knowledge of the chemical and physical properties of the individual components of the propellant is inadequate to describe quantitatively the behavior of the total propellant system. Thus, in spite of the imaginative and exhaustive work done on the mechanism and kinetics of thermal degradation of pure AP, the data obtained have been difficult to apply to the experimental observations of AP propellant deflagration. Such a lack of correspondence can be understood when one realizes that 1) the presence of the other ingredients in the propellant alters the degradation process of AP, and 2) the relative contribution of solid-phase and gas-phase reactions is a function of the operating parameters of the propellant system.

Of primary concern to the description of the mechanism of propellant deflagration and ignition has been the role of solid, solid-gas, and gas-phase reactions (the existence of a liquid phase adds another interface to the system). Several theoretical models on propellant combustion involve heat transfer from a two-stage flame to the solid surface undergoing endothermic reaction. The first stage of the flame consists of a

thin, premixed exothermic reaction zone fed by ammonia and perchloric acid generated by the decomposition of AP; in the second stage the combustion of fuel and oxidant molecules takes place under conditions which may involve diffusion- or kinetics-controlled regions. To provide the data necessary to relate this model to propellant combustion, we have carried out an experimental research program dealing with the kinetic processes of (1) the surface-phase reactions, and (2) the high-temperature flame reactions.

## TECHNICAL SUMMARY

To elucidate the processes controlling solid-propellant ignition, deflagration, and extinction, we have studied the solid and gas phase reaction kinetics of ammonium perchlorate in the presence of catalysts and organic fuels. The studies have demonstrated the important contribution made by condensed-phase reactions to the exothermic heat release rates of solid-propellant systems. These processes play a particularly important role in solid-propellant ignition. The pressure sensitivity exhibited by the burning rate of typical solid propellants is associated in part with the kinetics of the gas-phase reactions occurring in the combustion zone. To obtain a measure of the rate of the reactions at temperatures approaching those of the flame zone, we have developed the heterogeneous opposed-flow diffusion flame involving solid ammonium perchlorate and gaseous fuels as reactants. The data are analyzed by means of a theoretical model which yields the overall kinetics of the flame reactions, and provide a quantitative kinetic input into the analysis of solid-propellant combustion. The research results indicate the relative role of chemical and fluid-dynamic processes in the performance of operational propellants.

In summarizing the results, we present the major conclusion reached and list the technical reports or publications describing the relevant research.



## REPORTS AND PUBLICATIONS

### a. Surface Kinetics of Solid Propellants

1. S. H. Inami, W. A. Rosser, and H. Wise, "Heat-Release Kinetics of Ammonium Perchlorate in the Presence of Catalysts and Fuel," *Combustion and Flame* 12, 41 (1968).

The rate of heat release of ammonium perchlorate-fuel and ammonium perchlorate-catalyst mixtures under adiabatic conditions was studied as a function of temperature. In the presence of catalysts, the autocatalytic feature associated with nucleation of pure ammonium perchlorate disappears and the adiabatic reaction kinetics follow Arrhenius-type behavior. Studies made with ammonium perchlorate-fuel show that measurable heat release occurs at temperatures below the phase transition temperature of ammonium perchlorate and that the rate of heat generation per mass of material is greater than that of pure ammonium perchlorate. The rate of exothermic decomposition of pure ammonium perchlorate is unaffected by an increase in pressure. This observation suggests that the heat release is controlled by homogeneous or heterogeneous reactions in the condensed phase.

2. W. A. Rosser, S. H. Inami, and H. Wise, "Thermal Decomposition of Ammonium Perchlorate," *Combustion and Flame* 12, 427 (1968).

The decomposition of ammonium perchlorate and ammonium perchlorate-copper chromite mixtures has been studied in the temperature range from 250°C to 325°C. The products of decomposition were identified and the yield of each was established. Good recovery of N and Cl was achieved. The effect of atmosphere composition on the rate of decomposition was studied. The reaction mechanism proposed for the uncatalyzed decomposition involves the adsorbed dissociation products  $\text{NH}_3$  and  $\text{HClO}_4$ , self-protonation of  $\text{HClO}_4$  to yield the intermediate  $\text{ClO}_3^+$ , and oxidation of  $\text{NH}_3$  by  $\text{ClO}_3^+$ . The reaction mechanism proposed for the catalyzed decomposition involves the formation of the free radicals  $\text{NH}_4$  and  $\text{ClL}_4$ , decomposition of the radicals to  $\text{NH}_3$  and chlorine oxides, and subsequent oxidation of  $\text{NH}_3$ .

3. S. H. Inami, L. McCulley, and H. Wise, "Ignition Response of Solid Propellants to Radiation and Conduction," Combustion and Flame 13, 531 (1969).

Experimental measurements were carried out on the ignition response of solid propellants to radiative and to conductive heat transfer. The propellants were composed of ammonium perchlorate and different organic binders. The experimental results were interpreted in terms of a model including exothermic chemical reaction in the condensed phase of the propellant as the trigger for ignition. The heat release rates in the surface-coupled reactions were measured independently. A comparison of the ignition data demonstrated different response of the propellants to the two modes of ignition associated with the temperature/time history of the material.

4. S. H. Inami and H. Wise, "Catalytic Reactions of Dissociation Products of Ammonium Perchlorate," Combustion and Flame 13, 555 (1969).

Copper chromite catalyzes the decomposition of perchloric acid subliming off the surface of ammonium perchlorate until it changes. However in this process it tends to change its valence state from  $\text{Cr}^{\text{III}}$  to  $\text{Cr}^{\text{VI}}$ , with accompanying loss in catalytic activity. However it can undergo a redox cycle involving ammonia or the organic binder. This copper chromite plays a dual role in propellant kinetics. One as a decomposition catalyst for perchloric acid, and two, as an oxidation catalyst for ammonia and organic binder molecules.

5. S. H. Inami and H. Wise, "Oxidation of Ammonia Catalyzed by Mixed Oxides of Copper and Chromium," ONR Interim Report, 15 November 1969.

The product distribution ( $\text{N}_2$  vs.  $\text{N}_2\text{O}$ ) resulting from the catalytic oxidation of ammonia depends on the valence state of copper in the mixed-oxide catalyst. Over the temperature range studied  $\text{Cu}_2\text{O} \cdot \text{Cu}_2\text{O}_3$  favors  $\text{N}_2$  formation, while  $\text{CuCr}_2\text{O}_4$  favors  $\text{N}_2\text{O}$ .

6. S. H. Inami, Y. Rajapakse, R. Shaw, and H. Wise, "Solid Propellant Kinetics. I: The Ammonium Perchlorate-Copper Chromite-Fuel System," Combustion and Flame 17, 189 (1971).

In order to elucidate the rate processes controlling solid propellant ignition and deflagration, the kinetics of reaction has been studied at the interface of gaseous fuel and catalyst-containing ammonium perchlorate (AP). As representative fuels propylene, propane, and ammonia were employed, as a representative catalyst, the burning rate promoter copper chromite (CC: a mixture of cupric oxide and copper chromite) was used. Both the temperature of the solid AP-CC and the chemical composition of the gas were monitored in order to interpret kinetically the rates of fuel disappearance and product formation. The results indicate that the catalyst CC plays the dual role of accelerating the decomposition of AP and of promoting the oxidation of the fuel by heterogeneous reactions. These surface-catalyzed reactions at the surface of the solid AP-CC yield a net exothermic heat release whose magnitude is a function of the partial pressure of gaseous fuel and the concentration of CC catalyst.

b. Gas-Phase Kinetics of Solid Propellants

1. C. M. Ablow and H. Wise, "A Model Relating Extinction of the Opposed-flow Diffusion Flame to Reaction Kinetics," Combustion and Flame 22, 23 (1974).

A theoretical analysis is developed for the extinction of a homogeneous counterflow diffusion flame due to limitations in the reaction kinetics. With increasing mass flux of reactants into the diffusion flame a maximum in the consumption rate of fuel and oxidizer in the reaction zone occurs. The analysis shows that experimental measurements of the extinction conditions ("apparent flame strengths") can be used to evaluate quantitatively such kinetic parameters as the overall activation energy, the pre-exponential Arrhenius term, and the order of reaction. The theoretical model is applied to the propane-oxygen-nitrogen system, for which an activation energy of  $21 \pm 2$  kcal/mole is calculated on the basis of experimental flame extinction data.

2. C. M. Ablow and H. Wise, "Effect of Mass Oscillations on the Ignitability of a Heterogeneous System," ONR Interim Report, 15 November 1969.

For a heterogeneous system with heat generation by solid-gas reaction and heat loss by conduction-convection, the mass oscillations at the interface can play an important role in ignition. A theoretical analysis is carried out for such a system in which the ignition process is defined in terms of a reaction mechanism involving transition from kinetic to diffusive control. In a numerical example it is shown how the ignitability of a system varies with initial temperature, oscillation frequency, and amplitude. The analysis offers some indication of the importance of various parameters on the ignition and extinction of an oscillating heterogeneous system.

3. C. M. Ablow and H. Wise, "Solid Propellant Kinetics. II. Theoretical Analysis of the Heterogeneous Opposed Flow Diffusion Flame," ONR Interim Report 15 December 1971.

"A theoretical analysis is presented of the heterogeneous opposed flow diffusion flame (PFD). In such a system a gaseous reactant (G) impinges on a solid reactant (S) undergoing sublimation (or vaporization) and a diffusion flame is established at the stagnation point. With increasing mass flux of the gaseous reactant ( $m_G$ ) the mass flux of solid reactant ( $m_S$ ) grows until the total consumption rate of reactants reaches a limiting value due to limitations imposed by the kinetics of reaction. The analysis of the axi-symmetrical stagnation point flow with chemical reaction allows evaluation of the kinetics of chemical reaction at temperatures of interest to combustion processes. The theoretical development is applied to the solid-propellant deflagration of an ammonium perchlorate-catalyst-fuel system and the pyrolysis of solid polymers in an oxidizing atmosphere.

4. S. H. Inami and H. Wise, "Solid Propellant Kinetics. III. Experimental Study of the Opposed Flow Solid Propellant Diffusion Flame," ONR Interim Report, 15 December 1971.

The kinetics of high-temperature reactions associated with solid-propellant deflagration are studied quantitatively by means of the heterogeneous opposed flow diffusion flame.

In these experiments a cylindrical gas jet containing the gaseous fuel impinges on the surface of a solid propellant composed of ammonium perchlorate (AP) and copper chromite (CC) catalyst. A diffusion flame is established in the stagnation region formed by the two opposed flows of reactants. With increasing mass flux of gaseous fuel, the mass flux of solid AP/CC grows until a limiting condition is reached governed by the kinetics of reaction. Further enhancement in fuel flow does not result in any increase in the mass consumption rate of solid oxidizer. This condition of maximum reaction rate may be used in conjunction with a theoretical analysis to evaluate the kinetics of gas-phase reaction of the propellant system. The effects of various parameters on the kinetics of reaction were examined, including the catalyst concentration in the solid phase, the fuel concentration in the gas phase, and the temperature of the gaseous fuel. For the system AP/CC/methane an activation energy of 20 kcal/mole is evaluated for the gas phase reaction.

5. S. J. Wiersma and H. Wise, "Solid Propellant Kinetics. IV. Measurement of Kinetic Parameters in the Opposed Flow Solid Propellant Diffusion Flames," ONR Interim Technical Report, 20 December 1973.

To examine the gas-kinetics parameters pertinent to the flame reactions of ammonium perchlorate (AP) based propellants we have employed the heterogeneous opposed flow diffusion flame. In this combustion system a diffusion flame is formed in the stagnation region between a gaseous stream of fuel and an opposing stream of oxidizer originating at the solid surface of AP. With increasing fuel flux the steady-state mass flux of AP reaches a value at which the kinetics of reaction limit the consumption of reactants. This limiting condition provides information on the gas phase kinetic parameters of the combustion system. Both the composition of the solid oxidizer and the gaseous fuel were varied in the experimental studies. The effects of different catalysts and solid fuels were examined on the burning rate characteristics of the solid phase. A number of gaseous hydrocarbon fuels were used. Based on the results kinetic expressions are derived for the overall combustion progress in the diffusion flame of solid propellants based on AP.

6. C. M. Ablow and H. Wise, "Solid Propellant Kinetics. V. Fuel-Oxidizer Reaction Rates from Heterogeneous Opposed Flow Diffusion Flame," ONR Interim Report, December 1974.

A theoretical model is presented relating the gas dynamics and chemical kinetics of the opposed flow diffusion flame formed in the stagnation region between two opposing streams of gaseous reactants, one originating from the surface of a subliming solid, such as ammonium perchlorate. At low gas flows the regression rate of the solid is controlled by the physical properties of the system, including the net heat of gasification, the heat of combustion, and the transport parameters. At high gas flows a limiting solid regression rate is attained due to reaction-rate limitations that cause incomplete combustion of the reactants. The theoretical model developed for the heterogeneous opposed flow diffusion flame allows interpretation of the limit in solid regression rates in terms of global reaction kinetics. Calculations have been carried out for a range of parameters, including net heats of gasification and activation energies. For the AP-propylene system the experimental data can be fitted to a second-order gas-phase reaction rate with an activation energy of  $37.1 \pm 1$  kcal/mole and a preexponential coefficient of  $10^{13} \text{ cc} \cdot \text{mol}^{-1} \text{ sec}^{-1}$ .